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Use of off-line gel permeation chromatography–normal-phase liquid chromatography for the determination of polycyclic aromatic compounds in environmental samples and standard reference materials (air particulate matter and marine sediment)

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ABSTRACT

A method involving two levels of fractionation, semi-preparative gel permeation chromatography (GPC) and normal-phase liquid chromatography (NP-LC), and capillary gas chromatography with flame ionization and nitrogen–phosphorus detection coupled with mass spectrometry, was developed for the determination of polar substituted aromatic compounds (PACs) in environmental matrices. A GPC clean-up procedure (BioBeads SX-12–dichloromethane) efficiently removed lipidic matter from organic extracts, yielding an enriched PAC fraction. NP-LC (μPorasil) of that fraction provided a selectivity based on chemical classes and moderate to high recoveries for standard PAC. The application of this method to environmental samples and reference materials, air particulate matter (NIST 1649) and marine sediment (HS-4), demonstrated the validity of the procedure for the determination of polycyclic aromatic hydrocarbons (PAHs) from both qualitative and quantitative points of view. Further, a variety of aromatic ketones, quinones and aldehydes (oxy-PAHs) were determined in both matrices.

INTRODUCTION

The occurrence of polar substituted aromatic compounds (PACs) in the environment is of major concern because most of their chemical classes are carcinogenic [1]. Hence, the risk assessment associated with their occurrence requires the determination of environmental levels in the different compartments. However, whereas analytical procedures for the determination of polycyclic aromatic hydrocarbons (PAHs) in environmental samples are well established [2,3], methods for PACs require further research. In fact, because they usually occur at concentration levels several orders of magnitude lower than the corresponding parent PAHs, their characterization in environmental matrices requires multistage enrichment and fractionation techniques. In addition, the application of bioassay-directed fractionation strategies to environmental samples has revealed that a large proportion of the direct-acting mutagenicity can be accounted for by the PAC containing fractions [4,5].

Consequently, we have focused our attention on the development of a procedure for the determination of PACs in several environmental matrices, namely marine sediments and urban particulate matter. Previous workers studies have used normal- [6-8] and reversed-phase [9,10] liquid chromatographic (LC) methods to fractionate components in environmental extracts because they are fast and

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provide higher efficiencies than column chromatographic fractionation [11,12] or acid–base partitioning [13].

Although reversed-phase analytical LC is widely used, its usefulness at the semi-preparative level is limited by the low solubility of these complex organic mixtures in aqueous mobile phases [14]. On the other hand, an advantage of normal-phase LC is its selectivity, which allows the separation of PACs according to chemical functionalities [14], whereas the monomeric reversed-phase selectivity is mainly based on the number of aromatic carbon atoms in the case of the parent PAHs. Further, alkyl substitution in reversed-phase chromatography causes an appreciable increase in retention due to the decreased solubility in the polar mobile phase [15].

The approach described here is based on the use of sequential fractionation techniques of completely different selectivity. It includes the removal of the lipidic material by semi-preparative gel permeation chromatography (GPC), further fractionation of the aromatic-containing fraction (GPC-2) by semi-preparative normal-phase liquid chromatography (NP-LC) and capillary gas chromatography (cGC) with flame ionization (FID) and nitrogen–phosphorus detection (NPD) or cGC–mass spectrometry (cGC–MS) for the characterization of the PAC containing fractions. The validation of this methodology was performed with the analysis of two standard reference materials (SRMs) with certified PAH contents. Further, a wide variety of PACs, namely, aromatic ketones, quinones, aldehydes coumarins and nitroarenes, were identified in these SRMs and in environmental samples.

EXPERIMENTAL

Materials

Pesticide grade dichloromethane, hexane and isooctane were obtained from Baker (Phillipsburg, NJ,USA). Acetonitrile and methanol were HPLC grade (Teknokroma, Sant Cugat, Spain). 2-Nitrofluorene, 2-aminofluorene, 1-nitropyrene, acridine, naphthalene-1,4-dione and 9*H*-fluoren-9-one were purchased from Aldrich and Sigma (Steinheim, Germany). 7*H*-Benz[*de*]anthracen-7-one, benz[*a*]-anthracene-7,12-dione, benzo[*a*]fluorenone, pyrene-*x*,*y*-dione and 1-naphthol were a gift from Professor Milton L. Lee (Brigham Young University, Provo, UT, USA). Other standards were available in our laboratory.

Urban air particulate matter (NIST 1649) and marine sediment (HS-4), both with certified values for several PAHs, were obtained from the National Institute of Science and Technology (Gaithersburg, MD, USA) and the National Research Council (Halifax, NS, Canada), respectively. A sediment sample was collected with a Reineck box corer 2 km offshore near Barcelona. The sampled superficial sediment was wrapped in aluminium foil and frozen until analysis. Air particulate matter was collected in a Whatman GF/A (20.5 x 25.4 cm) glass microfibre filter using a HI-VOL sampling system (MC.V., Collbató, Spain). Samples were collected in a heavily trafficked square in Barcelona City 8 m above the street level. Filters were replaced every 24 h.

Extraction

SRMs (2.0 g of NIST 1649, 31.3 g of HS-4) and environmental samples (24-h filter and 30 g of freeze-dried sediment) were extracted with dichloromethane (5 x 15 ml and 5 x 30 ml, respectively) by sonication in glass centrifuge tubes, which is considered to be the most efficient method for these samples and artifact formation is minimized [16]. Extracts were evaporated nearly to dryness at reduced pressure and filtered through a glass-microfibre filter (Whatman GF/F) prior to chromatographic analysis.

Chromatographic fractionation

GPC. Filtered extracts (100 mg nominal mass) were injected into a Rheodyne (Cotati, CA, USA) valve (150 μl). A stainless-steel column (500 x 10 mm I.D.) packed with styrene–divinylbenzene copolymer (200–400 mesh) (Bio-Beads SX-12, Bio-Rad Labs., Richmond, CA, USA) was used with dichloromethane as the mobile phase at flow rate of 1 ml/min as reported elsewhere [17].

NP-LC. Standard solutions or GPC-2 fraction (15 mg) in dichloromethane were fractionated through a normal-phase semi-preparative column (300 x 7.8 mm I.D.) packed with 10-μm μPorasil (Waters Assoc., Milford, MA, USA). Injection was performed via high-pressure valve (Rheodyne) equipped with a 50-μl loop.

A high pressure pump (Kontron, Zürich, Switzerland) delivered mobile phase at a flow-rate of 4.5 ml/min. A UV-VIS detector (254 nm) (Varian, Sunnyvale, CA, USA) and fluorescence detector (λ_{ex} 254 nm and λ_{em} 390 nm) (Perkin Elmer, Norwalk, CT, USA) were coupled in series. The elution programme started isocratically with hexane for 5 min, followed by a linear gradient of 1%/min of dichloromethane for 5 min and then a linear gradient of 4%/min of dichloromethane for 25 min and held isocratically at 100% dichloromethane for 10 min. Subsequently, a linear gradient of 10%/min of acetonitrile and held at these conditions for 5 min, then a step back to 100% dichloromethane (5 min) and 100% hexane for 5 min was applied. The column was re-equilibrated with 100% hexane for 15 min before the next injection. Eight fractions were collected using a Gilson (Middleton, WI, USA) fraction collector (Fig. 1). The column was backflushed with methanol as described previously [6] and the eluate was collected as fraction nine, following the last injection of each sample fractionation.

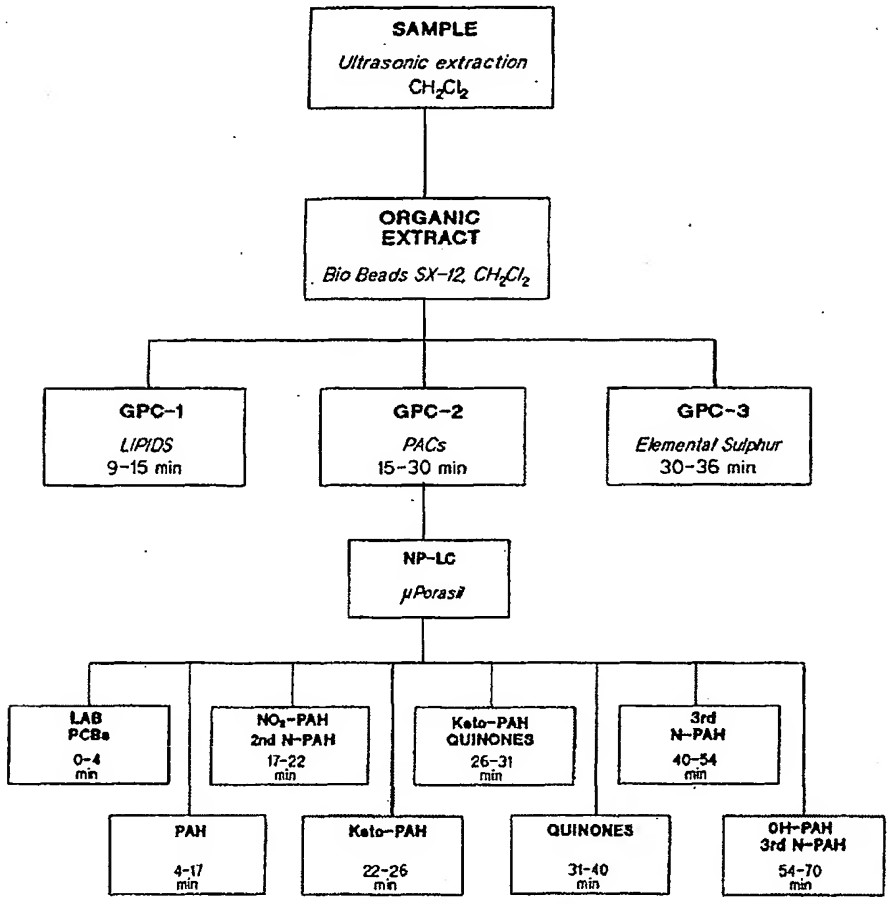

Fig. 1. Fractionation scheme. Compound-class identification as follows: LAB = long chain alquilbenzenes; PCB = polychlorobiphenyls; PAH = polycyclic aromatic hydrocarbons; NO_2-PAH = nitro substituted polycyclic aromatic hydrocarbons; 2nd N-PAH = secondary nitrogen heterocycles; Keto-PAH = polycyclic aromatic hydrocarbons with one carbonyl group; 3rd N-PAH = tertiary nitrogen heterocycles; OH-PAH = hydroxy substituted polycyclic aromatic hydrocarbons.

NP-LC fractions were evaporated nearly to dryness at reduced pressure, transferred to vials and blown down to dryness with a gentle stream of nitrogen. Blanks and spiked samples were processed in the same way as real samples.

Chromatographic Analyses

CGC. NP-LC fractions were analysed by cGC using a Carlo Erba (Milan, Italy) 5300 Mega series equipped with a split–splitless injector and with (FID) and (NPD), interfaced to a Nelson–Perkin-Elmer (Norwalk, CT, USA) data system. A fused-silica capillary column (30 m x 0.25 mm I.D.) coated with DB-5 (0.25 μm film thickness) (J & W Scientific, Folson, CA, USA) was used. Hydrogen was the carrier gas at linear velocity of 50 cm/s. The column temperature was programmed from 60 to 300°C at 6°C/min and the final temperature was held for 15 min. The injector, FID and NPD temperatures were held at 300, 330 and 310, respectively. Fractions from I to IV were analysed as solutions in isooctane, and in dichloromethane (FID) or ethyl acetate (NPD) for more polar fractions. Determinations of PAHs were accomplished as described elsewhere [18]. Nitrogen-containing PAHs were determined by cGC–NPD, using 9-nitroanthracene, 1-nitropyrene, 6-nitrochrysene and 6-nitrobenzo [*a*]pyrene.

cGC–MS. cGC–electron impact (EI) (70 eV) MS analyses were performed in a Hewlett-Packard Model 5985A quadrupole instrument interfaced to a Model 9825A data system. The injector, ion source and mass analyser temperatures were held at 300, 180 and 120°C, respectively. Helium was used as the carrier gas (30 cm/s) and scans were obtained every 0.86 s. The mass axis was calibrated with perfluorotributylamine using fragments at *m/z* 69, 219 and 502. Other chromatographic conditions were identical with those described for the cGC analysis. Positive identifications were made by injection of authentic standards and tentative identifications by the PBM algorithm search in the Wiley library.

Oxy-PAHs were determined by cGC–MS using 9*H*-fluoren-9-one, benzo[*a*]fluorenone, 7*H*-benz [*de*]anthracen-7-one, anthracene-9,10-dione and benz[*a*]antracene-7,12-dione as external standards in the multiple-ion detection (MID) and single-ion monitoring (SIM) modes for the air particulate matter and marine sediments, respectively. The SIM mode was performed using the molecular ion of these compounds as a diagnostic (*m/z* 180, 208, 230 and 258) with 2.0 cycles/s and a dwell time of

TABLE I

RETENTION AND RECOVERY BEHAVIOUR OF SELECTED STANDARD PAC BY NP-LC

Compound	t_R (min)	Fraction	Recovery (%)[a]
Octacosane	–[b]	I	79
Anthracene	6.4	II	–
Benzo[*ghi*]perylene	7.2	II	98
Coronene	7.5	II	–
2-Nitrofluorene	17.3	III	112
Carbazole	19.2	III	86
1-Nitropyrene	20.8	III	100
Naphthalene-1,4-dione	29.3	V	104
7*H*-Benz[*de*]anthracen-7-one	31.0	V	87
2-Aminofluorene	33.4	VI	36
Pyrene-*x*,*y*-dione[c]	37–40	VI	–
Acridine	50.4	VII	64
1,8-Naphthalic diacid anhydride	50–52	VIII	–
4-Nitrophenol	52–54	VIII	–
1-Naphtol	54.2	VIII	40

[a] Recovery experiments were perfomed at μg level.
[b] – Not determined.
[c] Mixture of : -3,8-, -8,3- and -8,10- isomers.

100 ms. Compound identification from the mass fragmentograms was accomplished by comparison with previously reported retention indices [19]. Aldehydes and coumarins were determined using the same response factor as for structurally related oxy-PAHs.

RESULTS AND DISCUSSION

The fractionation scheme applied is illustrated in Fig. 1. In the first level, organic extracts were fractionated into three fractions by semi-preparative GPC with dichloromethane. In previous work [17], we demonstrated the usefulness of this chromatographic system for the clean-up of environmental samples, allowing the removal of co-extractable lipidic material from PACs. The latter eluted in the fraction GPC-2 (15–28 min) with a recovery range from 75 to 100% depending on the chemical class of the PAC.

In this work, a separation scheme based on NP-LC using a silica gel μPorasil column, which allows the separation according to the different classes of PACs [14], was investigated (Fig. 1). The mobile phase composition and gradient programming were designed to optimize the resolution between PAHs, nitro-PAHs, oxy-PAHs, 3rdN-PAHs and hydroxy-PAHs. In this regard, Matsunaga [20] evaluated the separation of PAHs and PACs on several polar chemically bonded normal-phase (amino, nitro and cyanopropyl substituents) and silica gel. Although the amino phase had better selectivity and column stability, it is not suitable for carbonylic PAH analysis, as these compounds can react with the amino groups in the LC stationary phase to form Schiff bases [21].

On the basis of the retention time data for a standard mixture, the cut-off points between fractions were determined. This mixture was injected periodically in order to evaluate the change in reproducibility of retention times due to column deactivation.

Recoveries from NP-LC and retention time data for this mixture are summarized in Table I. Generally a good resolution between the standard compounds analysed was observed (Table II), although an overlapping between secondary nitrogen aromatic heterocycles (2ndN-PAHs) and nitro-PAHs is apparent. With nitrogen-containing PAHs, the retention times increase according to basicity. In this regard, it has been reported that basic nitrogen heterocycles are strongly retained on the μPorasil stationary phase owing to intense acid–base interactions of the basic nitrogen with the acidic silanol groups on the silica surface [14, 22] (t_R carbazole < t_R 2-aminofluorene < t_R acridine, $pK_a = -1.9$, 4.64 and 5.58, respectively).

The most interesting range of retention times on the NP-LC trace is that corresponding to the moderately polar fractions, where nitro- and oxy-PAHs, among other compounds, are eluted. In order to improve their resolution, a slow gradient of dichloromethane in hexane was applied. As far as the standard compounds are concerned, compound-class separation predominated. However, a slight overlapping between different chemical classes of PACs was observed with real samples, which was accounted for by a slight contribution of the number of aromatic carbons to the retention of PACs. This is the case with aromatic ketones and nitro-PAHs, but owing to the selective detection techniques used in analyse for these compounds, their

TABLE II

SELECTIVITY (α) ACCORDING TO PAH SUBSTITUTION ON NP-LC

Compound Class	PAHs	Nitro-PAHs	Keto-PAHs	Quinone	2ndN-PAHs	3rdN-PAHs
Nitro-PAHs	2.7					
Keto-PAHs	3.9	1.5				
Quinone	4.6	1.9	1.3			
2ndN-PAHs	3.0	1.1	1.3	1.5		
3rdN-PAHs	7.9	2.9	1.6	1.7	2.6	
Hydroxy-PAHs	8.5	3.1	2.2	1.8	2.8	1.1

simultaneous determination was possible, provided that the concentration ranges were comparable. Finally, the latest eluting class of PACs are hydroxy-PAHs owing to strong hydrogen bonding on the silica surface [14].

The recoveries were over 80% for most of the compounds analysed. The lowest recovery was found for hydroxy-PAHs, probably because these compounds were eluted among fractions 8 and 9, and fraction 9 was not considered in recovery determination. This polar fraction represents of 2% of the total mass of the extract of the marine sediments and 10–20% in case of air particulate matter samples.

Another group of compounds with moderate recoveries are the nitrogen-containing PAHs, especially the amino-PAHs, but this could be due to the instability of these compounds.

Application to environmental samples and standard reference materials

We evaluated the applicability of the two-step fractionation approach (Fig. 1) to environmental samples and marine sediment (HS-4, coastal sedi-

TABLE III

ANALYSIS OF URBAN PARTICULATE MATTER (UPM), NIST 1649, MARINE SEDIMENT (MS) AND HS-4 STANDARD REFERENCE MATERIALS

Peak No.	Compound	Concentration (μg/g)[a]				
		UPM	NIST 1649	MS	HS-4	
Polycyclic aromatic hydrocarbons						
1	Phenanthrene[b]	1.37	3.41 ± 0.05		0.27	(0.45 ± 0.15)
2	Anthracene	0.26	0.38 ± 0.2	0.06	0.06 ± 0.002	(0.14 ± 0.07)
3	3-Methylphenanthrene[b]	0.84	0.49 ± 0.2	0.10	0.08 ± 0.02	
4	2-Methylphenanthrene[b]	1.01	0.57 ± 0.3	0.13	0.07 ± 0.01	
5	4*H*-Cyclopenta[*def*]phenanthrene	0.44	0.10 ± 0.01	0.07	0.02 ± 0.01	
6	9-Methylphenanthrene	0.75	0.37 ± 0.2	0.11	0.08 ± 0.02	
7	1-Methylphenanthrene[b]	0.71	0.25 ± 0.01	0.10	0.04 ± 0.01	
8	Fluoranthene[b]	4.55	6.04 ± 0.8 (7.1 ± 0.5)	0.48	1.01 ± 0.2	(1.25 ± 0.2)
9	Acephenanthrylene	2.56	0.12 ± 0.01		0.07 ± 0.01	
10	Pyrene[b]	6.59	6.68 ± 0.8	0.37	0.80 ± 0.1	(0.94 ± 0.12)
11	Methylpyrenes					
12	Benzo[*ghi*]fluoranthene[b]	6.68	0.96 ± 0.3		0.21 ± 0.01	
13	Benzo[*c*]phenanthrene[b]		0.36 ± 0.05		0.12 ± 0.01	
14	Benz[*a*]anthracene[b]	5.35	2.13 ± 0.5 (2.6 ± 0.3)	0.28	0.47 ± 0.1	(0.53 ± 0.05)
15	Chrysene + triphenylene[b]	7.74	4.26 ± 0.2	0.17	0.68 ± 0.2	(0.65 ± 0.08)
16	Methylchrysenes					
17	Benzofluoranthene[c]	5.48	11.63 ± 1.5	0.23	1.46 ± 0.3	
18	Benzo[*e*]pyrene[b]	8.67	4.21 ± 0.6	0.11	0.45	
19	Benzo[*a*]pyrene[b]	9.64	3.32 ± 0.6 (2.9 ± 0.5)	0.11	0.60 ± 0.2	(0.65 ± 0.08)
20	Perylene[b]	1.85		0.02	0.32 ± 0.02	
21	Indeno[7,1,2,3-*cd*]chrysene	3.36	0.39 ± 0.04		0.14 ± 0.01	
22	Indeno[1,2,3-*cd*]pyrene[b]	10.0	3.81 ± 0.6 (3.3 ± 0.5)	0.13	0.62 ± 0.03	(0.51 ± 0.15)
23	Dibenzo[*a,h*]anthracene[b]		0.60 ± 0.05		0.13 ± 0.01	(0.12 ± 0.05)
24	Benzo[*b*]chrysene[b]		0.28 ± 0.01		0.05 ± 0.01	
25	Benzo[*ghi*]perylene[b]	26.2	4.31 ± 0.8 (4.5 ± 1.1)	0.24	0.54 ± 0.02	(0.58 ± 0.22)
26	Anthracene[b]	2.34	0.12 ± 0.02		0.09 ± 0.01	
27	Dibenzopyrenes					
28	Coronene	12.8	3.91 ± 0.4	nd[d]	0.14 ± 0.01	
Nitroarenes						
29	1-Nitropyrene[b]	0.11	0.18 ± 0.02	nd	nd	
	6-Nitrobenzo[*a*]pyrene[b]	nd	nd		0.34 ± 0.11	

TABLE III (*continued*)

Peak No.	Compound	Concentration (μg/g)[a]			
		UPM	NIST 1649	MS	HS-4
Polycyclic aromatic ketones					
30	9*H*-Fluoren-9-one[b]	0.37	0.30 ± 0.03	0.022	0.012 ± 0.001
31	C_3-9*H*-Fluoren-9-one	0.02	0.02 ± 0.01	0.002	0.001
	C_2-9*H*-Fluoren-9-one	0.01	0.02 ± 0.01	0.001	0.001
	C_1-9*H*-Fluoren-9-one	0.01	0.02 ± 0.005	0.001	0.002
32	C_2-9*H*-Fluoren-9-one	0.02	0.01 ± 0.002		
33	Anthrone[b]	0.001	0.02 ± 0.00	0.008	0.002
34	Xanthone[b]	0.005	0.07 ± 0.02		
35	4*H*-Cyclopenta[*def*]phenanthrene-4-one[b]	0.41	0.17 ± 0.05	0.003	0.13 ± 0.002
36	Benzo[*a*]fluorenone[b]	1.36	1.89 ± 0.3	0.020	0.834 ± 0.09
37	Benzo[*c*]fluorenone	0.63	0.42 ± 0.05	0.024	0.016 ± 0.003
38	Benzo[*b*]fluorenone	0.72	1.57 ± 0.02	0.004	0.010 ± 0.002
39	7*H*-Benz[*de*]anthracen-7-one[b]	2.35	1.31 ± 0.02	0.001	0.021 ± 0.005
40	Benzopyrenone isomer	0.30	nd	0.004	0.004
41	Benzopyrenone isomer	–[c]	0.19 ± 0.02	nd	0.0004
Polycyclic aromatic quinones					
42	Antracene-9,10-dione[b]	0.41	0.22 ± 0.04	–	0.009
43	Benz[*a*]anthracene-7,12-dione[b]	0.79	7.465 ± 1.1	0.005	0.159 ± 0.02
Polycylic aromatic aldehydes					
44	Formylphenanthrene-anthracene isomer	–	0.02 ± 0.001	nd	nd
45	Formylphenanthrene-anthracene isomer	–	0.03 ± 0.002	nd	nd
Coumarines					
46	5*H*-Phenanthro[4,5-*bcd*]pyran-5-one[b]	0.84	0.16 ± 0.02	nd	nd
47	Coumarin (MW = 246)	–	0.17 ± 0.05	nd	nd

[a] Certified values in parentheses [23–25]. Procedural relative standard deviations (n = 3) are indicated as ± values.
[b] Positive identification by co-injection with an authentic standard, otherwise identifications are based on EI mass spectra, positive response in selective detectors (NPD) and retention indices.
[c] [*b*], [*j*] and [*k*] isomer mixture for the NIST 1649 and our determination but for HS-4 includes only [*b*] and [*k*] isomers.
[d] nd, Not detected.
[e] –, Not determined.

ment) and airborne particulate matter (NIST 1649, urban particulate matter) SRMs, which represent two environmental matrices with high levels of biogenic interferences. These SRMs have certified contents of some PAHs.

The levels of different chemical classes of PACs identified and the certified values are given in Table III. The identification of oxy-PAHs, reported for the first time in these SRMs is note-worthy.

The chromatographic profiles corresponding to the PAH fraction are shown in Fig. 2. From the quantitative point of view, a deviation from certified levels below the 20-30% was observed for marine sediment sample with low levels of PAHs, whereas for air particulate matter with higher levels the deviation was about the 10–15%. The highest deviation occurs with benzofluoranthene isomers ([*b*], [*j*] and [*k*]), probably owing to the lack of chromatographic resolution between these isomeric compounds in our chromatographic system. However, in the HS-4 reference material, the certified value corresponds to a mixture of [*b*] and [*k*] isomers therefore explaining the observed quantitative differences.

On the other hand, taking into account that the relative standard deviation of the whole analytical procedure is in the range 15–20% (n = 3), the values obtained in this study fall within the range of most of the certified values.

In addition, this fractionation procedure allowed the identification of several other classes of PACs, namely aromatic ketones, aldehydes, quinones and

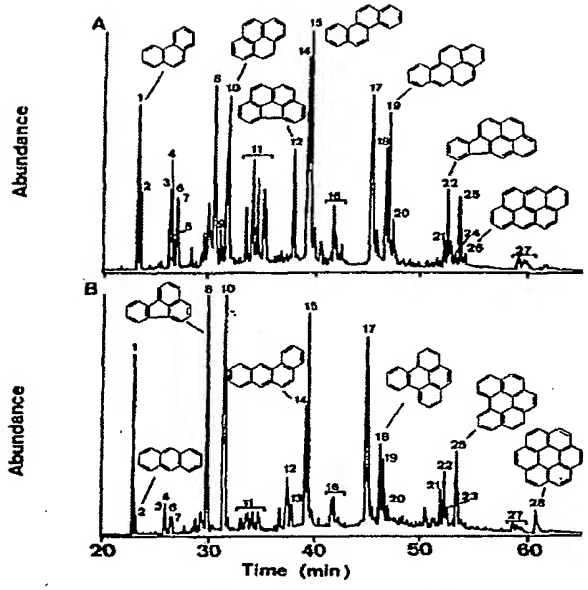

Fig. 2. cGC–MS profile of PAH fraction of SRMs isolated from (A) marine sediment (HS-4) and (B) air particulate matter (NIST 1649). For compound identification, see in Table III.

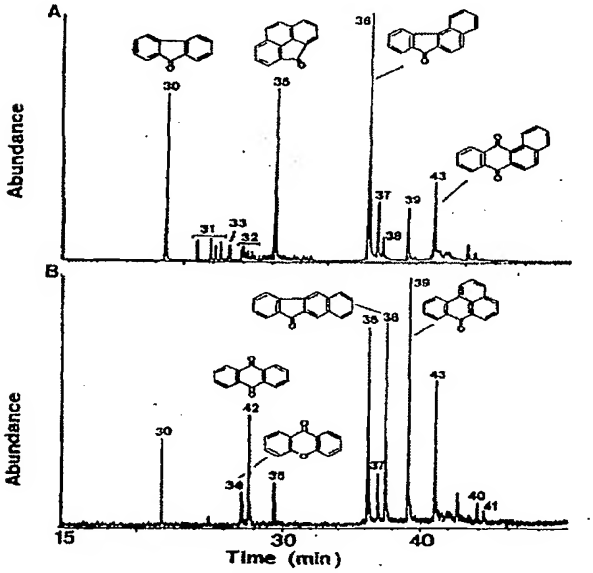

Fig. 3. cGC–MS profile of SRM fractions V and VI isolated from (A) marine sediment (HS-4) and (B) air particulate matter (NIST 1649). For compound identification, see Table III.

TABLE IV

LIMITS OF DETECTION (LOD) (ng/g) OF PACs IN SRM

Compound	NIST 1649	HS-4
PAHs[a]		
Pyrene	8.8	0.58
Benzo[*ghi*]perylene	28	1.8
Nitroarenes[b]		
9-Nitroanthracene	7.2	–
1-Nitropyrene	4.7	–
Ketones		
7*H*-Benz[*de*]anthracen-7-one	43[c]	0.008[d]

[a] FID.
[b] NPD.
[c] MS (MID).
[d] MS (SIM).

nitroarenes, in these samples, present at lower concentrations. The cGC–MS profiles obtained for the SRMs are shown in Fig. 3. Important differences between the two environmental matrices were evident. First, higher levels of these compounds were detected in the air particulate matter according to their sources. Second, as far as nitroarenes are concerned, only 1-nitropyrene was detected in NIST 1649, at a concentration similar to that reported by Ramdahl *et al.* [24] for the same sample. On the other hand, the penta- and hexa-fused aromatic ring nitroarenes are predominant in sediment samples (Table III).

Finally, the detection limits for the PAC classes were calculated, taking into account the recovery for the overall analytical procedure (extraction, GPC–NP-LC fractionation and the determination technique) (Table IV). The selection of the final determination was based on the concentration levels and on the interferences in the same fraction. In this regard, although electron-capture detection exhibited a higher sensitivity than NPD or MS for the determination of nitroarenes and oxy-PAHs, the presence of interferences precluded its application.

Further, the lower detection limit obtained with HS-4 can be accounted for by larger amount of sample extracted, as the concentration levels of PACs in sediments are lower than those in air particulate matter (Table III). Therefore, the detection and determination of oxy-PAHs in sediments required the application of the SIM detection mode.

CONCLUSIONS

A method for the simultaneous determination of several chemical classes of PACs has been developed. The main interest is the combination of GPC as a clean-up step prior to compound fractionation, yielding an enriched PAC fraction, which was further fractionated by NP-LC according to chemical classes. Finally, the applicability of these techniques to the determination analysis of PAHs and the intermediate polarity PACs in two environmental matrices has been demonstrated.

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